Comment on "Direct Observation of Charge Ordering in Magnetite Using Resonant Multiwave X-Ray Diffraction"

The study of the Verwey transition in magnetite has been a matter of intense study during the last years [1,2]. The mechanism proposed by Verwey [3] was the charge localization and ordering of the electrons at the iron octahedral sites giving rise to an ordered sequence of Fe^{3+} and Fe^{2+} ions. Recent x-ray diffraction and resonant x-ray scattering at the iron K edge have strongly modified this description. The charge disproportion between octahedral iron sites is far from one electron with a distribution of fractional charges that is multimodal instead of bimodal [4,5].

In a recent Letter, S-C Weng *et al.*[6] present a resonant multiwave x-ray diffraction method and they assert that this method provides a more direct and effective way to determine the charge disproportion in magnetite. We here show that this assertion is inaccurate and misleading. Our first objection to this Letter is that no sequence of the charge ordering is proposed. The authors claim on a direct determination of charge disproportion without establishing between which atoms the disproportion occurs. In addition to this criticism, we will put in evidence several errors or inconsistencies in the methodology and results presented by the authors in the commented Letter.

(1) The authors claim that self-normalized three-wave to two-wave (002) diffraction intensity ratio automatically cancels the self-absorption effect. This should be correct if the experiments were performed across the absorption iron K edge, but the experiment was only performed up to 7120 eV (see Fig. 4 of the Letter), which is below the absorption edge of magnetite [7]. Therefore, the whole experiment is performed below the iron K edge and the self-absorption effect is negligible.

(2) The authors incorrectly assume that the involved reflections are sensitive to charge ordering. On one hand, reflection (002) is sensitive to the trigonal anisotropy of the octahedral sites but not to the charge ordering, as is clearly shown in [8,9]. This makes the resonant intensity of this reflection strongly depend on the azimuthal angle when rotating around the scattering vector. Any treatment of this reflection must consider these properties which are not taken into account by the authors. On the other hand, none of the reflections (3,1,1), (3,1, − 1) and (− 3,−1,1) are sensitive to the charge ordering because their structure factors do not contain differences between octahedral iron sites [10].

(3) The subtraction of the intensity dependence with photon energy of two reflections, which are not sensitive to charge ordering, and, in addition, they are measured below the absorption edge, cannot provide valuable information on any charge disproportion.

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